# Metal Complexes of Phthalocyanines in Polymers as Suitable Materials for Optical Limiting

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**Summary:** Germanium and tin phthalocyanines containing peripheral and axial different substituents were synthesized. Thin multi-layer films of PMMA and PVC containing monomolecular phthalocyanines were obtained by spin-coating on glass substrates. The phthalocyanines were characterized by their absorption spectra. Optical limiting properties of the phthalocyanines in solution and in polymer films were investigated.

**Keywords:** optical limiting; phthalocyanines; polymer films; solid devices

## Introduction

Organic materials displaying large nonlinear optical responses are of major interest in the development of photonic and optoelectronic technologies due to their fast response time, large nonlinear susceptibilities and also comparatively low fabrication costs.[1–5] Practical NLO applications include the use of organic materials with optical limiting (OL) properties. The transmission for light of an ‘‘ideal’’ optical limiter optical limiter is high at normal light intensities and low for intense light intensities. The output energy of a limiter rises linearly with input until a threshold is reached (Figure 1). Then the output energy is clamped at a given value for any larger input energy. Generally the research is focused on optical shielding, specifically the protection of human eyes, optical elements and optical sensors from intense laser pulses.

The main mechanisms to achieve optical limiting are nonlinear absorption and nonlinear refraction. The theoretical background for the effect of optical limiting was recently reported.[1–5] Most important to achieve OL is the sequential two-photon absorption and filling of the involved electronic levels. A five-level diagram can be used to discuss nonlinear absorption of phthalocyanines (Pc) (Figure 2). After illumination a photon goes from $S_0$ to $S_1$ which is followed by decay to $S_0$ or lower $T_1$ state. The molecule in the $S_1$ or $T_1$ state may absorb another photon and be excited to a higher singlet level $S_2$ or triplet level $T_2$, respectively. If the molecule has an excited state ($S_1$ or $T_1$) absorption cross section ($\sigma_{ex,S}$ or $\sigma_{ex,T}$) larger than the ground state cross section ($\sigma_0$) including high populations, the effective absorption of the molecule increases and *reverse saturable absorption* (RSA) occurs (values of $\sigma_{ex,S}/\sigma_0$ or $\sigma_{ex,T}/\sigma_0 > 1$). Molecules with high intersystem crossing rates from $S_1$ to $T_1$ can give high $T_1$–$T_2$ transitions. In fact, phthalocyanines can have a high $T_1$ quantum yields, and values of $\sigma_{ex,T}/\sigma_0 > 1$ (some times between 10 and 20) were determined.[1–5]

Among the large number of NLO absorbers, phthalocyanines have recently ermerged as most promising materials due to their extended delocalized $\pi$-electron structure leading to strong excited state absorptions, high triplet yields, fast NLO response times and easy processing. Through both axial (via the central metal) and peripheral (at the ligand) substitutions

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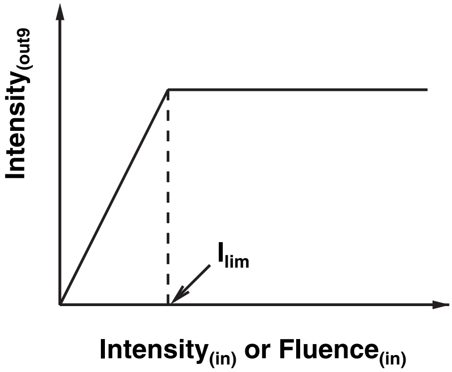

*Figure 1.*
Ideal behavior of an optical limiter.

the basic Pc structure has led to a large control of NLO including OL properties.[4–8] Various other materials such as fullerenes, carbon nanotubes and porphyrins find interest for practical optical limiting applications (see references cited in [4]).

The linear UV-visible absorption spectra of phthalocyanines are characterized by the Q band region at λ ~ 680 nm, the B band region at λ ~ 350 nm and low or nearly no absorption between the B and Q bands. For phthalocyanines the triplet absorption maximum was found between the Q and B band, a region implying the cross section of the excited state is at a maximum of around 520 nm. A range of NLO parameters can be used to characterize the optical limiting properties of phthalocyanines. The properties are described by the linear absorption coefficient $\alpha_o$, the effective intensity dependent effective nonlinear absorption coefficient $\beta_1$, the effective third order susceptibility $I_m\{\chi^{(3)}\}$, the ratio of the excited triplet and ground state cross sections absorption $\sigma_{ex,T}/\sigma_0$ giving the $\kappa$ value, the energy density at which the molecule saturates $F_{Sat}$.

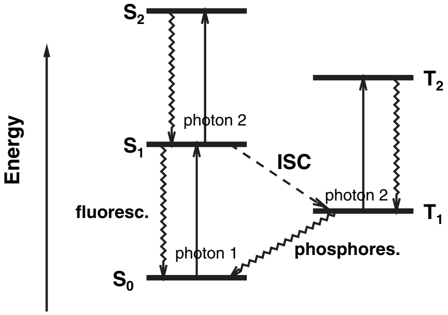

*Figure 2.*
Five-level energy diagram accounting for the nonlinear absorption behaviour. S and T are different singlet and triplet states, respectively.

The OL properties of a large variety of phthalocyanines have recently been characterized in solution.[4–8] However for practical applications it is essential to investigate the OL of phthalocyanine compounds in solid state. Phthalocyanines embedded in a sol-gel host or poly(methylmethacrylate) were previously reported.[9] This study details the NLO characterization of a variety of phthalocyanines embedded in some host polymers. The aim of this research is to realize solid state metal phthalocyanine optical limiters with similar properties to those in solution.

## Experimental

### Materials and Methods

Solvents were purified by distillation. Methylcyclohexanone is a mixture of isomers (Merck-Schuchardt). All other chemicals were commercially available and used without further purification. The following commercially available organic polymers were used: poly(methylmethacrylate) PMMA (Acros Organics) $\overline{M_w} = 350000$ and $\overline{M_n} = 60000$, poly(vinylchloride) PVC (Aldrich) $\overline{M_w} = 106000$ and $\overline{M_n} = 60000$. As carriers for thin films commercial glass slides size 20 × 20 mm and thickness 1 mm from Menzel-Glaser were used. A spin coater CONVAC 1001S was used for solid state film preparation. The resulting film thicknesses were measured with a Dektak 3030T instrument. UV-vis spectra were recorded on a Perkin Elmer Lambda 2 to measure the linear optical properties of phthalocyanines in solution and solid state.

### Synthesis

The synthesis and structural characterization of the investigated phthalocyanines

(Pc) will be described elsewhere.[10] For example, the following compounds were prepared: dichlorogermanium(IV) and dichlorotin(IV) 2,9,16,23-tetrakis-(4-formylphenoxy)-phthalocyanine (**1**), dichlorotin(IV) 2,9,16,23-tetrakis-(4-nitrophenoxy) phthalocyanine (**2**), bis(3,5-di-*tert*-butylphenoxy)-germanium(IV) 2,9,16,23-tetranitrophthalocyanine (**3**), dichlorotin(IV) hexadecafluorophthalocyanine (**4**), difluorotin(IV) hexadecachloro-phthalocyanine (**5**) and bis(3,5-di-*tert*-butylphenoxy)germanium (IV) hexadeca-chlorophthalocyanine (**6**) (Fig. 3).

Exemplary, the main steps for the synthesis of **1** are summarized: 4-nitrophthalonitrile was reacted with *p*-formylphenol in the presence of potassium carbonate in dimethylsulfoxide for 72 hours to give 4-formylphenoxyphthalonitrile. Cyclotetramerization of 4-formyl-phenoxyphthalonitrile in 1-pentanol in the presence of strong base (DBU) results in the metal-free tetra(*p*-formylphenoxy) substituted phthalocyanine. The metallations of this metal free Pc were carried out in a high-boiling aromatic solvent (quinoline in the case of **1** (M = Ge) and 1-chloronaphthalene in the case of **1** (M = Sn)) with the metal tetrachlorides $SnCl_4$ and $GeCl_4$, respectively. All Pcs were analytically characterized.

### Film Preparation by Spin-Coating

For the preparation of polymer solutions 1.3 g PVC were dissolved in 10 mL methylcyclohexanone under stirring for 24 h. In the case of PMMA 1.5 g of this polymer was dissolved in 10 mL methylcyclohexanone by treatment in an ultra sonic bath for 12 h. Solution of phthalocyanines were prepared by dissolving $3 \times 10^{-6}$ mol of a phthalocyanines in 0.5 mL toluene or chloroform in order to obtain a concentration of $6 \times 10^{-3}$ mol $L^{-1}$. Solutions for coating were prepared by mixing 0.5 mL of Pc solution with 2.5 mL of a polymer solution to obtain a concentration between $1 \times 10^{-3}$ mol $L^{-1}$. The solutions were gently stirred slowly for ~20 min in order to get homogeneous solutions and to minimize air bubble formation. Monolayer films were prepared by dropping approximately 0.3 mL of a solution containing the dissolved polymer and the Pc onto a glass plate rotated with

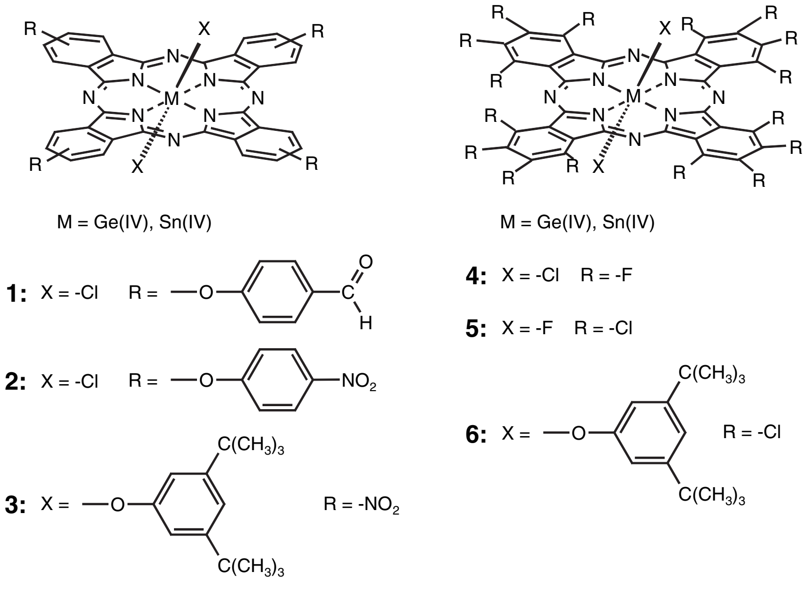

*Figure 3.*
Structure of some prepared phthalocyanines.

speed of 3000 rpm for 5 min. Afterwards the layer was dried at 100 °C for 1 h. Multilayer films were obtained by a sequential deposition and spin casting process.

### Optical Limiting Measurements

The optical limiting response of the samples was measured using a Z-scan architecture with open aperture.[4,11] The experiments were performed using ~6 ns Gaussian pulses from a Q switched Nd:YAG laser. The beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. The irradiation at 532 nm is then a near-resonant excitation.

Measurements in solution were carried out in a quartz cuvette of 1 mm path length containing Pcs in a concentration of $\sim 4 \times 10^{-4}$ mol $L^{-1}$. For polymer films the conditions were described above.

## Results and Discussion

### Preparation and Linear Optical Properties of Phthalocyanines in Solution and Thin Films

Phthalocyanines are very promising materials for optical limiting (OL) in the visible and NIR spectral range, because of their appropriate photophysical properties (high transmission between $\lambda \sim 400$ and 600 nm, strong excited state absorptions, high triplet yields, long excited-state life times). Important is that varying the central metal cation and the substituents one can tune the photophysical properties. Tendencies to improve OL are as follows:[4,5]

- Heavy metal cations in the ligand (increase of intersystem crossing rate from $S_1$ to $T_1$),
- axial substituents (reduce aggregation and enhance of perpendicular dipole moment),
- peripheral substituents with strong especially electron-withdrawing effect (alteration of the electronic properties, variation of transition dipole moment).

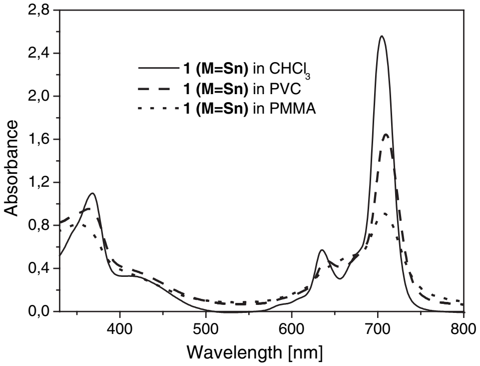

***Figure 4.***
Absorption spectra of **1** (M = Sn) in chloroform solution, in PMMA (6 layers, thickness 180 μm) and in PVC (7 layers, thickness 180 μm).

Based on these results germanium(IV) and tin(IV) complexes bearing electron-withdrawing substituents in peripheral and axial positions were synthesized.[10] Some examples of prepared Pcs are shown in Figure 3.

Figure 4 contains exemplary an optical spectrum of a Pc characteristic for a totally monomolecular dissolved metal phthalocyanines with the characteristic Q band at $\lambda \sim 690$ nm ($\pi$-$\pi$ transition) and Soret band at $\lambda \sim 380$ nm. The Q-band represents absorption of light and consequently excitation of electrons from the highest occupied molecular orbital (HOMO), namely the $a_{1u}$ ($\pi$), to the lowest unoccupied molecular orbital (LUMO), namely the $e_g$ ($\pi^*$). Furthermore, the transition from $a_{2u}$ to $e_g$ results in the Soret-band formation. In the long wavelength region of visible light the position of the Q-band is very sensitive against Pc-Pc interactions. Aggregation of Pc molecules results in a broad band of lower intensity at $\lambda \sim 620$ nm.

Visible absorption spectra are a valuable tool to study the distribution of phthalocyanines in solution. The same situation is valid for Pcs in thin films which can be considered as a solid solvent. In the long wavelength region of visible light the position of the $\pi$–$\pi^*$ transition called Q-band is

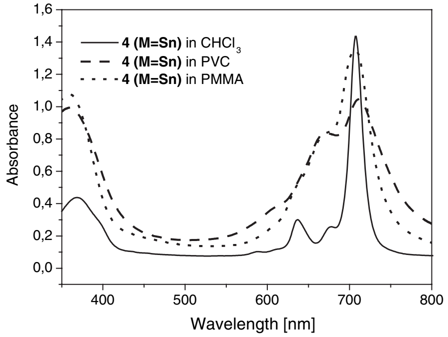

***Figure 5.***
Absorption spectra of **4** (M = Sn) in chloroform solution, in PMMA (6 layers, thickness 180 μm) and in PVC (7 layers, thickness 190 μm).

very sensitive against Pc-Pc interactions and is also influenced by a polar environment of a host lattice. Single and multilayer films in PMMA or PVC on glass were obtained by spin-coating from methylcyclohexanone solutions of Pcs and polymers. Absorption spectra in transmission of the spin-coated films of **1** in polymers show the Q-band at $\lambda \approx 690$ nm which is characteristic for a monomolecular distributed Pc as in solution (Figure 4). The absorptions are slightly broadened compared to solution spectra. In PMMA the absorptions are slightly broader than in PVC. The absorption spectra of **2** with *p*-nitrophenoxy peripheral substituents in solution and in solid state are quite similar to that of compound **1**. For both compounds the absorption spectra of films in PVC are more bathochromic shifted than in films of PMMA. For films of **4** (M = Sn) in PMMA and PVC some part of the Pc exist in an aggregated state (shoulder at ~620 nm, Figure 5). In contrast, compound **6** (M=Ge) having bulky axial groups, di(*tert*-butyl)phenoxy, shows a strong bathochromic shift of the Q band to 736 nm. These bulky axial substituents reduce aggregation also in polymer films.

In contrast, if films are prepared from solution by drop-coating, the films often show a shift of the main absorption to around 620 nm which indicates stacked aggregated Pcs. The formation of aggregates of Pcs in drop-coated films is due to the slow evaporation of the solvent (48 h) which results in step-wise interaction of Pcs and formation of aggregates/particles. In contrast, the spin-coating process with quick evaporation of the solvent did not result in formation of aggregates (Figure 5). But it should be mentioned that also by spin-coating some part of the Pcs may aggregate. This depends on the kind of Pc and polymer. If, for example, the less polar poly(styrene) is used, mainly aggregation of Pcs occurs also in spin-coated films.

### Nonlinear Optical Properties of Phthalocyanines in Solution

A very convenient and fast experimental method to measure materials for optical limiting is the open aperture Z-scan technique.[4,11] The samples were dissolved in appropriate organic solvents (Table 1) at

***Table 1.***
Some selected linear, calculated nonlinear optical coefficients and optical limiting parameters of standards from the literature and investigated phthalocyanines 1–6 in solution.

| Compound | Conc./g L$^{-1}$ | $\alpha_o$/cm$^{-1}$ | $I_o$/GW cm$^{-2}$ | $\beta_1$/cm W$^{-1}$ | $F_{Sat}$/J cm$^{-2}$ | $\kappa$ ($\sigma_{exT}/\sigma_o$) |
|---|---|---|---|---|---|---|
| $t$Bu$_4$PcInCl[a,b] | 0.5 | 0.53 | 0.5 | 4.4e-8 | 24.2 | 27.4 |
| PdPc(C$_6$H$_{13}$)$_8$[a,b] | 1.0 | 2.60 | 0.5 | 9.6e-8 | 2.1 | 5.9 |
| **1** (M = 2H)[c] | 0.5 | 3.65 | 0.7 | 1.3e-8 | 30.7 | 5.7 |
| **1** (M = Ge)[c] | 0.5 | 1.02 | 0.4 | 2.1e-8 | 14.2 | 13.0 |
| **1** (M = Sn)[c] | 0.5 | 1.02 | 0.5 | 2.9e-8 | 13.6 | 16.9 |
| **2** (M = Sn)[d] | 0.5 | 1.30 | 0.5 | 2.9e-8 | 7.7 | 10.2 |
| **3** (M = Ge)[c] | 0.5 | 4.05 | 2.9 | 9.0e-9 | | |
| **4** (M = Sn)[c] | 0.5 | 2.73 | 1.2 | 4.0e-8 | 12.9 | 7.3 |
| **5** (M = Sn)[e] | 0.5 | 2.57 | 0.4 | 1.5e-8 | 23.2 | 4.6 |
| **6** (M = Ge)[f] | 0.5 | | 2.8 | 2.3e-9 | | |

[a] Reference [4]. [b] Toluene. [c] Tetrahydrofurane. [d] Dimethylformamide.
[e] 1-Chloronaphthalene. [f] Chloroform.

***Table 2.***
Some selected linear, calculated nonlinear optical coefficients and optical limiting parameters of investigated phthalocyanines **1–6** in polymers.

| Compound, polymer | No. layers | Thickn./μm | $\alpha_o$/cm$^{-1}$ | $I_o$/GW cm$^{-2}$ | $\beta_1$/cm W$^{-1}$ | $F_{Sat}$/J cm$^{-2}$ | $\kappa$ ($\sigma_{exT}/\sigma_o$) |
|---|---|---|---|---|---|---|---|
| **1** M = Ge), PVC | 4 | 1 | 1900 | 0.7 | 6.0e-5 | 5.9 | 10.8 |
| **1** (M = Ge), PVC | 7 | 1.9 | 962 | 0.6 | 5.1e-5 | 5.3 | 10.4 |
| **1** (M = Sn) PVC | 4 | 1 | 1335 | 0.3 | 1.5e-5 | 20.2 | 10.9 |
| **1** (M = Sn), PVC | 7 | 2.3 | 688 | 0.4 | 1.7e-5 | 10.2 | 10.7 |
| **1** (M = Ge), PMMA | 3 | 1 | 1914 | 0.6 | 5.4e-5 | 11.6 | 12.0 |
| **1** (M = Ge), PMMA | 6 | 1.9 | 1110 | 0.7 | 3.9e-5 | 6.6 | 9.0 |
| **1** (M = Sn), PMMA | 3 | 1 | 1844 | 0.2 | 3.7e-5 | 6.1 | 6.7 |
| **1** (M = Sn), PMMA | 6 | 2.3 | 851 | 0.4 | 9.3e-6 | 15.3 | 8.0 |
| **2** (M = Sn), PVC | 4 | 0.9 | 1876 | 0.7 | 1.6e-4 | 2.9 | 13.7 |
| **3** (M = Ge), PMMA | 3 | 0.8 | 2980 | 0.3 | 8.7e-5 | 5.3 | 7.2 |
| **4** (M = Sn), PMMA | 3 | 0.8 | 2305 | 0.4 | 9.9e-5 | 6.3 | 10.4 |
| **6** (M = Ge), PVC | 4 | 0.8 | 3375 | 0.9 | 4.4e-4 | 2.1 | 9.6 |

concentrations of 0.5 g L$^{-1}$. The phthalocyanine solutions were put into a low-power (60 W) sonic bath for about 1 hour in order to obtain homogenous and complete dissolution. In a detailed theoretical study optical limiting devices built from reverse absorbers were described.[12] In this work for the evaluation of the optical limiting properties of the investigated Pcs the following parameters were determined (for more details see [4,5]) and are exemplary included in Tables 1 and 2:

- concentration of Pcs in solution (g L$^{-1}$) or thickness of films (μm),
- linear absorption coefficient $\alpha_o$ (cm$^{-1}$) at 532 nm,
- intensity of light at the focus $I_o$ (GW cm$^{-2}$),
- effective intensity dependent nonlinear absorption coefficient $\beta_1$ (cm W$^{-1}$),
- energy density at which the material saturates $F_{Sat}$ (J cm$^{-2}$),
- value of $\kappa$ which is the ratio $\sigma_{exT}/\sigma_o$ of the excited triplet state and ground state absorption cross section ($\kappa < 1$ saturable linear absorption occurs, $\kappa > 1$ reverse saturable absorption occurs which is necessary for OL).

Some of these parameters were used in the literature to estimate the effectiveness of optical limiting materials. In this report values of $\beta_1$, $F_{Sat}$ and $\kappa$ are taken into account. In solution $\beta_1$ ranges in the order of $10^{-10}$ to $10^{-8}$ cm W$^{-1}$, $F_{Sat}$ in the order of 5 to 150 J cm$^{-2}$ and $\kappa$ in the order of 2 to 27.[4] Two of the compounds with the best described OL properties are highlighted in Table 1: chloroaluminium tetra-*tert*-butylphthalocyanine ($t$Bu$_4$PcInCl) and palladium octahexylphthalocyanine (PdPc-$(C_6H_{13})_8$).[4] $t$Bu$_4$PcInCl exhibits the highest reported $\kappa$ value ($\kappa$ value for fullerene 5.2), but high $F_{Sat}$ and low $\beta_1$ values. In contrast the Pd compound shows higher $\beta_1$ and lower $F_{Sat}$ values, but a low $\kappa$ value. It is not easy to estimate which Pc will be the better optical limiter, and –important to mention- these compounds were not investigated in polymer films.

It can be seen from Table 1 that some of the investigated compounds in solution show a good combination between a relatively high absorption cross section $\kappa$ (<17), a low energy dependent saturation $F_{Sat}$ (>2.1 J cm$^{-2}$) and a relatively high effective nonlinear absorption coefficient $\beta_1$ (<5 cm W$^{-1}$). For **1** both, $\beta_1$ and $\kappa$ values, increase in going from $M = 2H < M = Ge < M = Sn$, whereas $F_{Sat}$ decreases. This is due to the heavy metal atom effect that the SnPc exhibits the best OL properties. This excellent combination of values makes the SnPc compound a candidate for the use as optical limiter. As for other Pcs the effective nonlinear absorption coefficient $\beta_1$ decreases slightly with increasing beam intensity $I_o$.[4] This is exemplary shown for **1** (M = Ge) in Figure 6. The optical limiting data plotted as normalized transmission as a function of incident energy per pulse for **1**

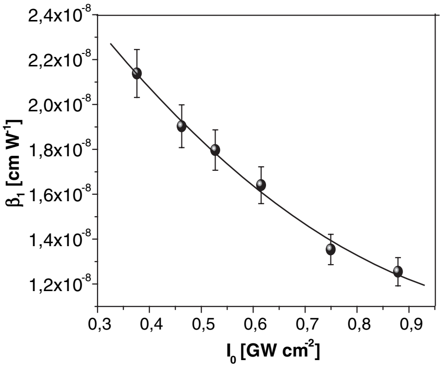

***Figure 6.***
Plot of the effective nonlinear absorption coefficient $\beta_1$ against the on-focus beam intensity $I_o$ for **1**(M = Ge).

are depicted in Figure 7. It is obvious that **1** (M = Sn) exibits the best nonlinear response in terms of transmission versus pulse-energy density while the metal free **1** (M = 2H) possesses the weakest response.

For the other compounds the same trend was observed. Compared to **1** (M = Sn) with formylphenoxy groups as substituents, compound **2** (M = Sn) with the more electron-withdrawing nitrophenoxy groups as substituents saturates at much lower $F_{\mathrm{Sat}}$ values. Compound **4** (M = Sn) containing 16 fluorine groups as substituents shows better OL properties than **5** (M = Sn) with 16 chlorine substituents (higher $\beta_1$ and $\kappa$, lower $F_{\mathrm{Sat}}$ values; see also Figure 8 for the plot of normalized transmission against pulse energy density). This is an effect of the strong electron-withdrawing effect of the fluorine groups. Bulky substituents in the axial positions improve the OL performances as seen comparing **6** (M = Ge) with **5** (M = Sn) (both compounds contain 16 chlorine groups). The bulky phenoxy groups in axial positions of **6** results in better values even that **6** contains M = Ge and **5** M = Sn.

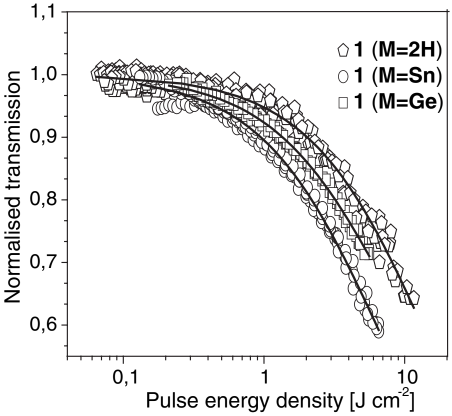

***Figure 7.***
Optical limiting plotted as norma-lized transmission against incident pulse energy density for **1** (M = 2H, Ge, Sn).

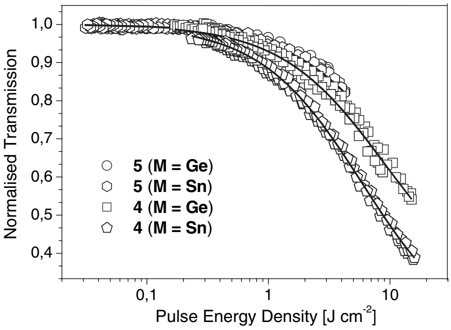

***Figure 8.***
Plots of normalized transmiss-ion against incident pulse energy density for **4** (M = Ge, Sn) and **5** (M = Ge, Sn).

## Nonlinear Optical Properties of Phthalocyanines in Thin Films of Polymers

Clear homogeneously coloured films of Pcs in polymers were obtained by spin-coating on glass plates. For each layer 0.3 mL of a methylcyclohexanone solution containing $1 \times 10^{-3}$ mol L$^{-1}$ of a Pc and 0.038 g PVC or 0.044 g PMMA were employed for spin-coating. Multi-layer devices were obtained by repeated spin-coating on the before prepared and dried films. Devices with 3 to 7 layers have thicknesses between 0.8 and 2,3 μm, respectively (Table 2). Figure 9 demonstrates nicely that the absorbance of monomolecular Pcs in the films increases continuously with increasing film thicknesses. Also compound **6** containing bulky phenoxy groups in axial positions is monomolecular included in polymers whereas

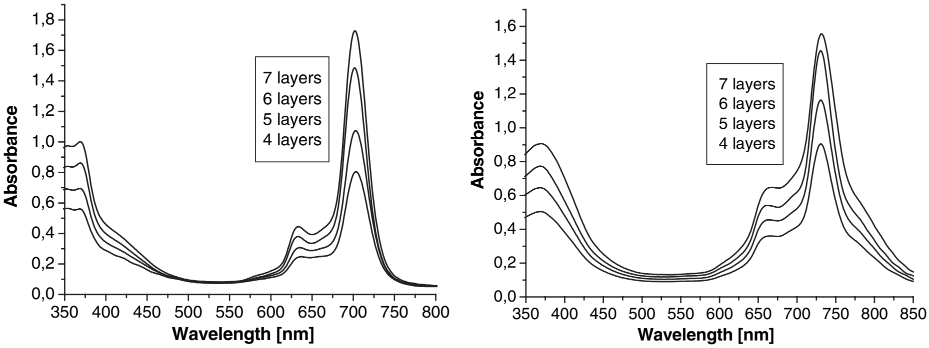

***Figure 9.***
Absorption spectra of multilayer thin films containing phthalocyanines in PVC. Left: **1** (M = Sn). Right: **6** (M = Ge).

with axial Cl groups some aggregation occurs (Figure 5, compound **4**).

All investigated Pcs exhibit nonlinear properties not only in solution but also in polymer films (Table 2). In general the OL properties of Pcs in polymers are often better compared to the solution properties. The $\kappa$ values for **1** (M = Ge, Sn) are comparable for 3- and 6-layer films in PMMA and for 4- and 7-layer films in PVC. This indicates that the formylphenoxy peripheral groups effectively suppress molecular aggregation, even at high concentration. But the lower $\kappa$ values in polymers compared to solution shows the influence of host lattice interactions which were also visible in the absorption spectra (Figure 4). On the other hand, the values of the linear absorption coefficient, $\alpha_o$, for polymeric Pc films are much higher than for Pcs in solution. In addition, the values of the effective nonlinear absorption coefficient $\beta_I$ are considerably higher for films than for Pcs in solution, which indicates that Pcs in polymers increase the magnitude of the imaginary nonlinear response at appropriate intensities.

Optical limiting plotted as normalized transmission against pulse energy density for multilayer films of **1** (M = Sn) embedded in PMMA and PVC is shown in Figure 10. It is seen that the magnitude of nonlinear absorption is slightly different for **1** in solid state samples and in solution. The magnitude of nonlinear absorption of films of compound **1** shows that the nonlinear optical response of this compound in PVC is better than in PMMA, and that thicker films due to higher Pc concentration led to a lower normalized transmission relative to the pulse energy than thinner films. It can be estimated considering the combination of OL values that **1** (M = Sn) is interesting for practical devices.

For compound **2** (M = Sn) the value of $\kappa$ is slightly lower but the value of $F_{Sat}$ is slightly higher in polymers comparing with the values in solution (Table 1, 2). Plots of the normalized transmission against the pulse energy density for compound **2** show the same trend as discussed for compound **1** (Figure 11): reduced transmission with increasing pulse energy in solid state compared to solution and in thicker films compared to thinner ones. Only 10% transmission occurs for **2** in polymers at a

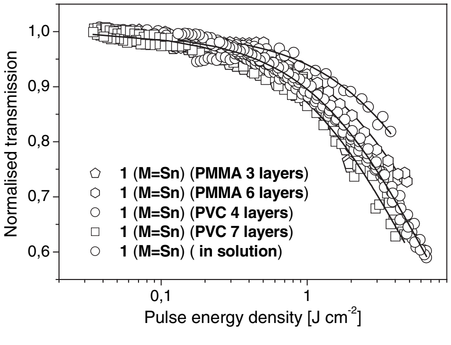

***Figure 10.***
Optical limiting plotted as norma-lized transmission against incident pulse energy density for **1** (M = Sn) in PMMA and PVC.

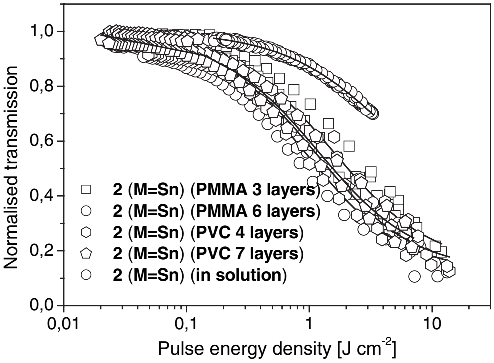

***Figure 11.***
Optical limiting plotted as normalized transmission against incident pulse energy density for **2** (M = Sn) in PMMA and PVC.

high energy density 10 J cm$^{-2}$. Also for compound **3** (M = Ge) it is seen from Figure 12 that the optical limiting properties in polymer films are improved compared to solution. The phthalocyanines **4** (M = Sn) and **6** (M = Ge) exhibit in polymer films a higher absorption cross section value $\kappa$ and a lower energy density saturation value $F_{\mathrm{Sat}}$ compared to solution (Table 1, 2). Also the plots of normalized transmission against pulse energy density (Figure 13) estimate that this material is interesting for practical OL devices.

## Conclusion

Taking into account results of optical limiting investigation in the literature about phthalocyanines in solution new phthalocyanines derivatives **1–6** were synthesized successfully. These compounds contain germanium(IV) or tin(IV) as central metal cation and peripheral and axial substituents with mainly electron-withdrawing properties. Some are bulky substituents to reduce aggregation of the metal complexes. Multilayer films of PVC and PMMA containing the phthalocyanines were obtained by spincoating on glass substrates. Absorption spectra were used to measure the linear optical properties. In solution and in polymer films most phthalocyanines are totally monomeric and not aggregated.

The optical limiting properties of the phthalocyanines in solution and in polymer films were measured by the open aperture Z-scan technique. All measurements were

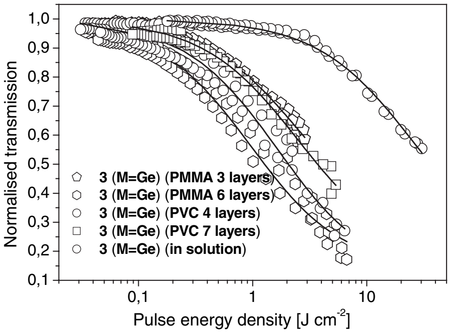

***Figure 12.***
Optical limiting plotted as norma-lized transmission against incident pulse energy density for **3** (M = Ge) in PMMA and PVC.

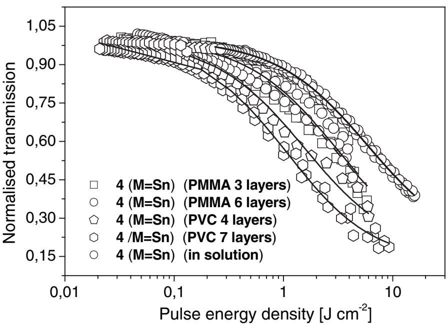

***Figure 13.***
Optical limiting plotted as norma-lized transmission against incident pulse energy density for **4** (M = Sn) in PMMA and PVC.

performed using 6 ns pulses from a Q-switched Nd:YAG laser. The laser was operated at its second harmonic, 532 nm, with a pulse repletion of 10 Hz. The compounds were characterized by the effective intensity dependent nonlinear absorption coefficient $\beta_1$, the energy density at which the material saturates $F_{Sat}$ and the value of $\kappa$ (ratio $\sigma_{exT}/\sigma_o$ of the excited triplet state and ground state absorption cross section). In solution especially the combination of values of compounds **1** (M = Sn) and **2** (M = Sn) makes them interesting for practical application. The optical limiting properties of the phthalocyanines in multi-layer films of PMMA and PVC are in most cases better compared to properties in solution and are often better in polymer films. Some devices exhibit excellent combination of $\beta_1$, $F_{Sat}$ and $\kappa$ values. Also the plots of normalized transmission against pulse energy density show that some devices are interesting for practical application.

*Acknowledgements:* This project was supported by the European Union Network under the contract HPRN-00020 and the Volkswagen Foundation under the grant I/78 204.

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